Automation and Methodology Development for Environmental and Biological Determination of Pu, Np, U and Tc

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Properties of Pu, Np, U and Tc

Nuclide	Isotope	Main origination	Half-life	Main production	Principal decay mode
Pu	^{238}Pu	Anthropogenic	87.7 y	NA and β decay of ^{235}U and ^{238}U	α
	^{239}Pu		2.4×10^{4} y	Bombardment of ^{238}U	α
	^{240}Pu		6.6×10^{3} y	^{239}Pu (n, γ) ^{240}Pu	α
	^{241}Pu		14.4 y	^{240}Pu (n, γ) ^{241}Pu	β^-
Np	^{237}Np	Anthropogenic	2.4×10^{6} y	NA and β decay of ^{235}U and ^{238}U	α
U	^{234}U	Natural	2.4×10^{6} y		α
	^{235}U	Natural	2.5×10^{5} y		α
	^{236}U	Anthropogenic	2.3×10^{7} y	^{235}U neutron activation (NA)	α
	^{238}U	Natural	4.5×10^{9} y		α
Tc	^{99}Tc	Anthropogenic	2.1×10^{5} y	^{235}U, ^{239}Pu fission product	β^-

Sources of Pu, Np, U and Tc in the environment

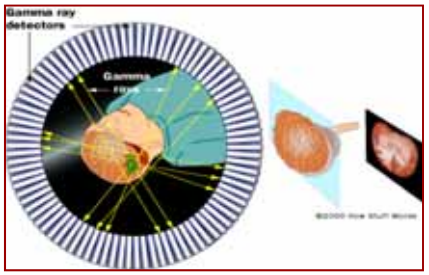
Nuclear weapons testing

Nuclear power plants

Pu isotopes,
^{237}Np, ^{99}Tc,
^{236}U

Nuclear reprocessing plants

Nuclear accidents



Nuclear medicine

Sources of Pu, Np, U and Tc in the environment

Sources of Pu and Np in the environment						
Source term	^{238}Pu, Bq	^{239}Pu, Bq	^{240}Pu, Bq	^{241}Pu, Bq	^{237}Np, Bq	^{240}Pu/^{239}Pu atomic ratio
Nuclear weapons testing	3.3×10^{14}	7.4×10^{15}	5.2×10^{15}	1.7×10^{17}	3.9×10^{13}	~0.19
Burn up of SNAP-9A	6.3×10^{14}	-	-	-	-	-
Thule, Greenland, 1968	-	1×10^{13}		-	-	-
Palomares, Spain	-	5.5×10^{10}		-	-	-
Chernobyl, 1986	3.0×10^{13}	2.6×10^{13}	3.7×10^{13}	5.5×10^{15}	-	~0.39
Sellafield reprocessing plant	1.2×10^{14}	6.1×10^{14}		2.2×10^{16}	-	-
La Hague reprocessing plant	2.7×10^{12}	3.4×10^{12}		1.2×10^{14}	-	-

Sources of Pu, Np, U and Tc in the environment

Sources of ^{99}Tc and ^{236}U in the environment	
Source term	**^{99}Tc released, Bq**
Sellafield nuclear reprocessing plant	1.72×10^{15}
La Hague nuclear reprocessing plant	1.54×10^{14}
Global weapons fallout (1940s-1970s)	1.40×10^{14}
Nuclear accident in Chernobyl	7.5×10^{11}
Estimated nuclear accident in Fukushima	$>2.5 \times 10^{11}$
Estimated medical application (^{99}Mo-^{99m}Tc generator)	$<2 \times 10^{10}$
Estimated nuclear power plants	$<1 \times 10^{10}$
Source term	**^{236}U released, Bq**
Natural	8.4×10^{10}
Anthropogenic	2.4×10^{15}

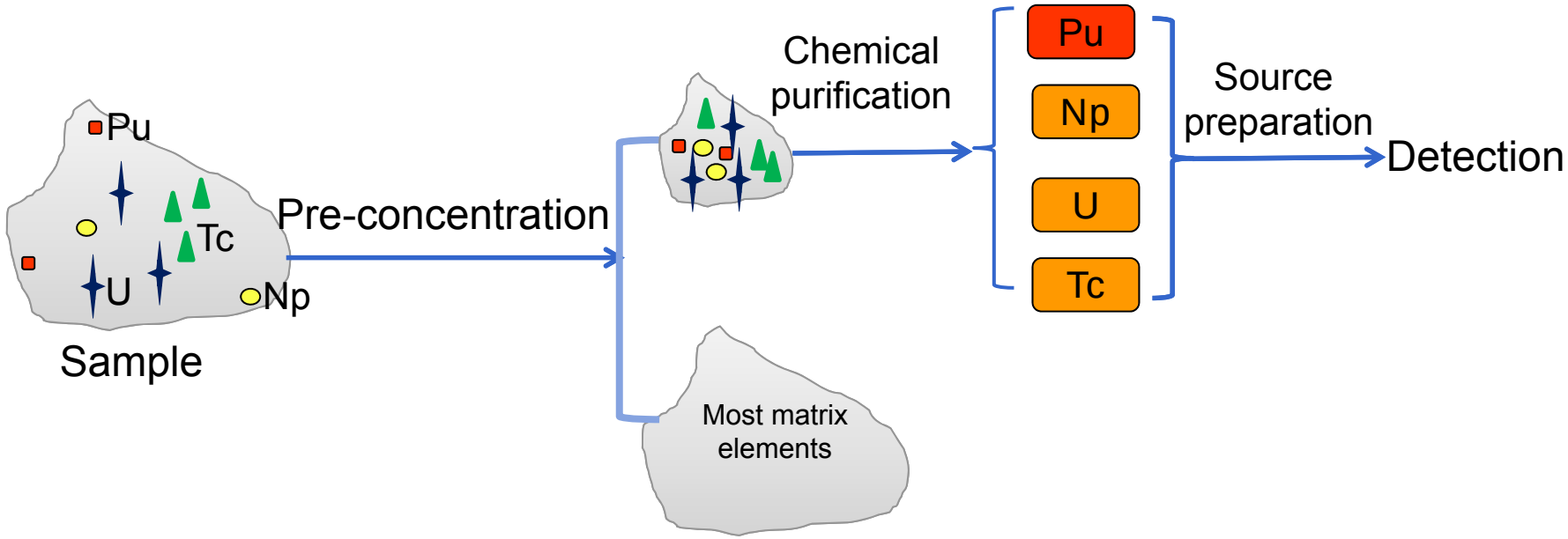
Significances of Pu, Np, U and Tc determination

1) Environmental risk assessment and monitoring
2) Nuclear emergency preparedness
3) Routine occupational health monitoring
4) Nuclear Forensics
5) Nuclear decommissioning and waste disposal
6) Radioecology and tracer studies

Distribution characters of Pu, Np, U and Tc in environmental and biological samples

1) Levels are very low and vary with location or sample type

2) Often coexist with matrix elements (Ca, Mg, Al, V, Ru, Mo…) and other interfering radionuclides (Th, Am, Cm…)



Traditional analytical methods for Pu and Np

Pre-concentration:

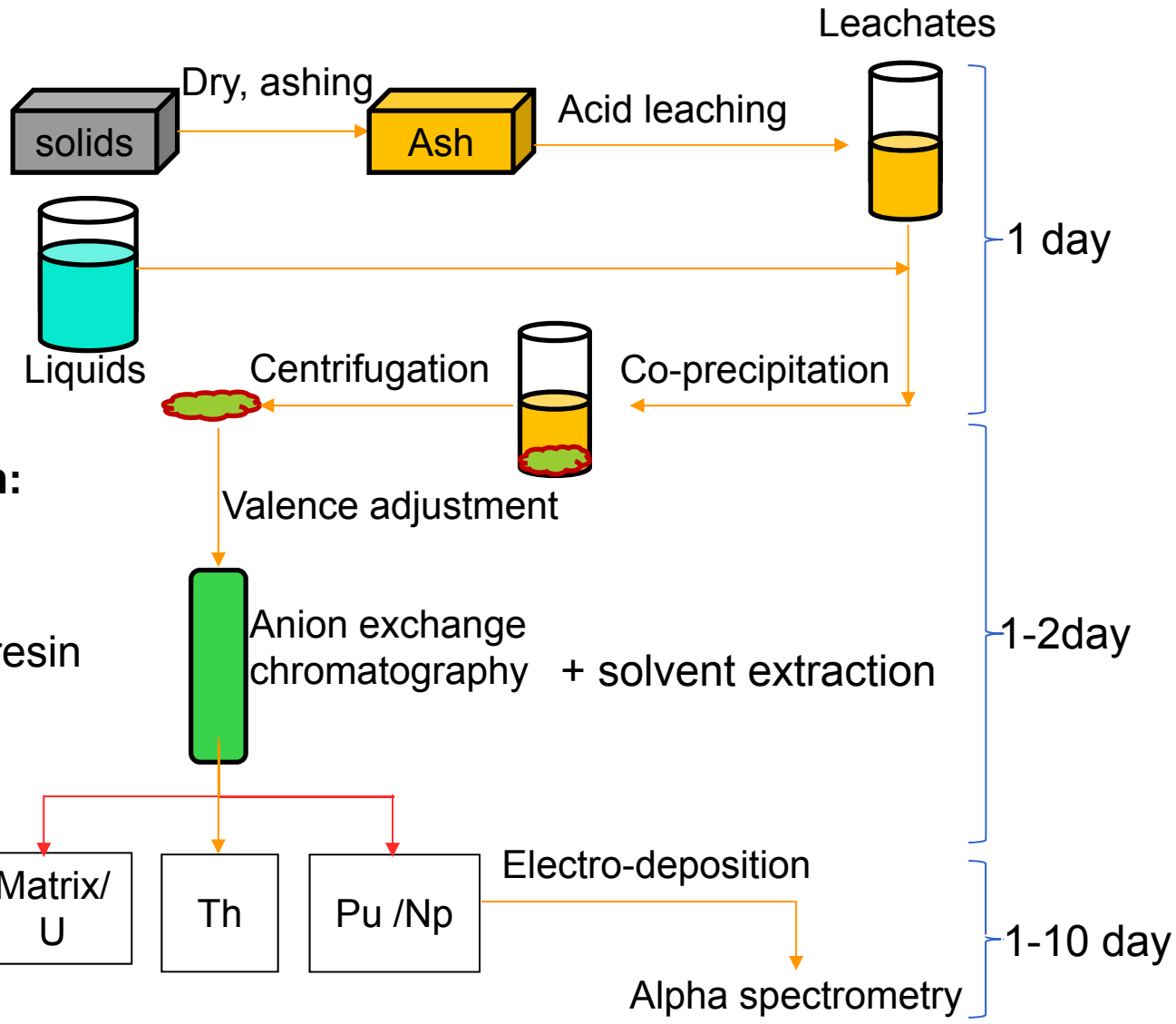
- 8-16 batchwise
- Fairly straightforward

Chemical purification:

- Lengthy
- High labor intensity
- High consumption of resin
- Organic waste

Detection:

- Long counting time
- High detection limit



Our objectives

1. Rapid determination of Pu, Np, U and Tc
2. Automation of the analytical procedure

Specific focuses:

i. Chemical purification

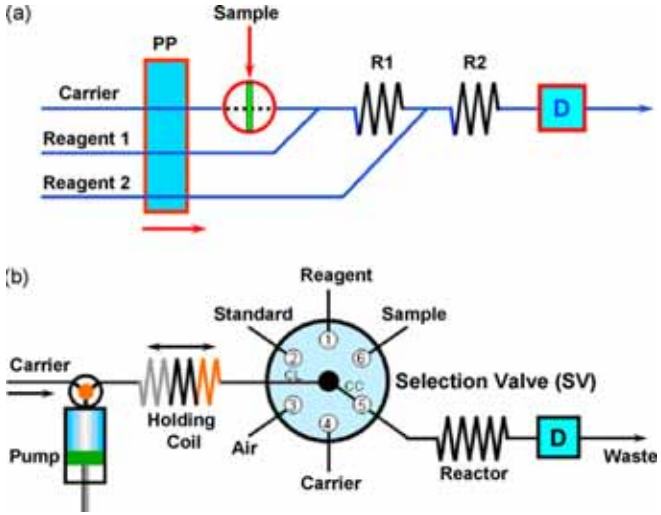
- Protocol simplification and optimization
- Automation

ii. Detection

- Mass spectrometry (ICP-MS, AMS)

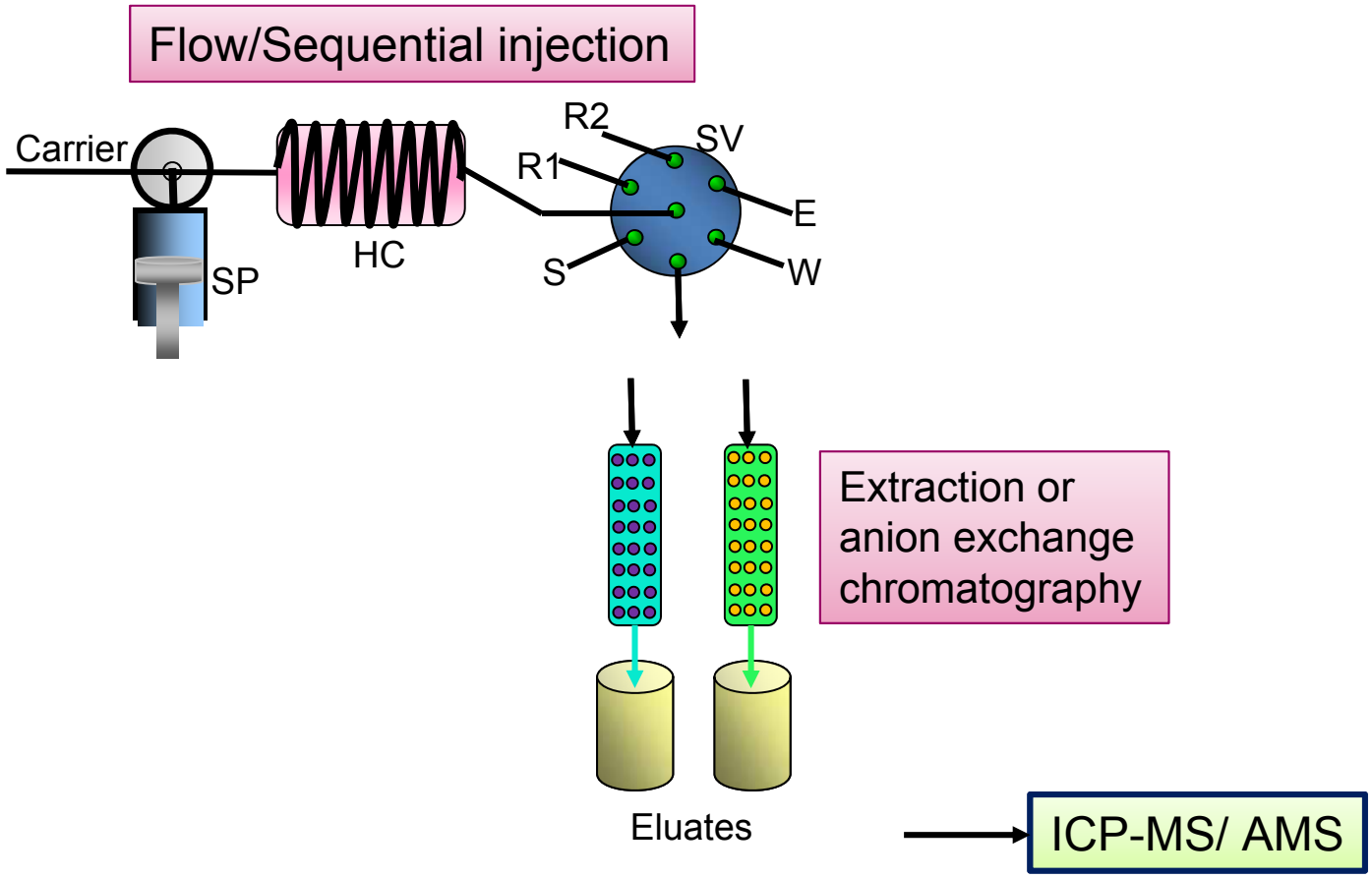
Automation techniques

- **Vacuum box**
- **HPLC**
- **Flow injection/Sequential injection**



Qiao, J. X., Hou, X. L., Miró, M., Roos, P. Analytica Chimica Acta. 2009, 652, 66-84.

Final strategies



Methods Development-Pu and Np

Environmental Samples:

- 0.5-200 g of soil, sediment or seaweed
- 50-200 L of seawater

Parameters optimized:

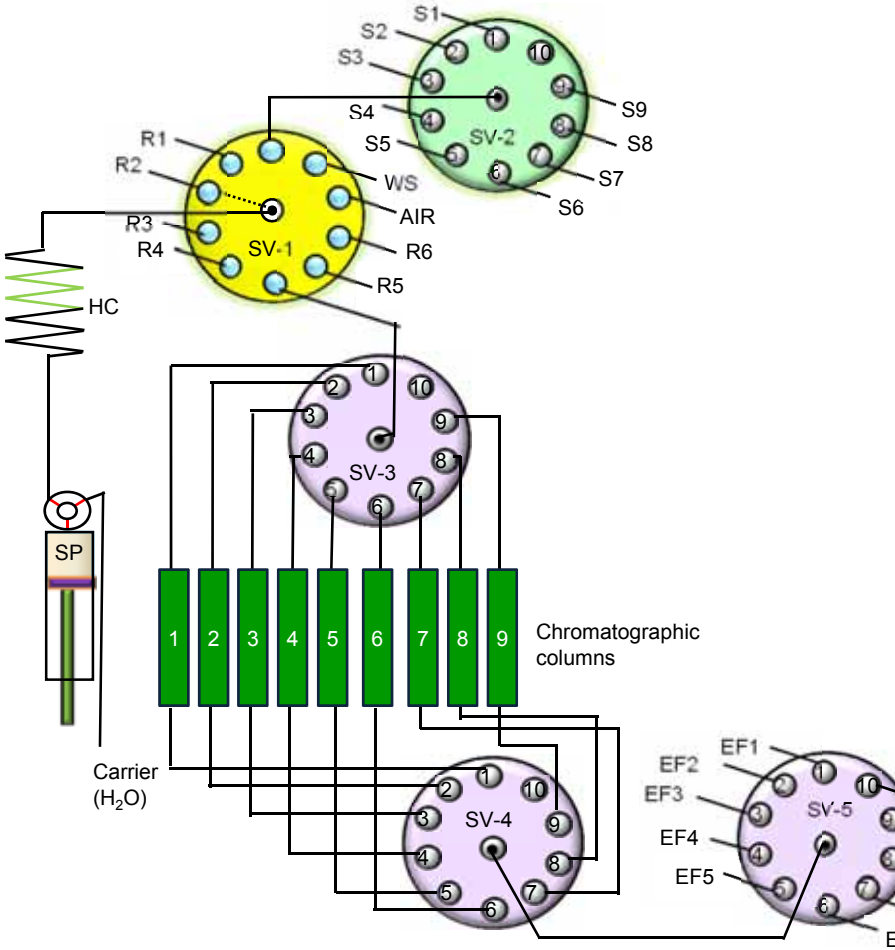
- Resin type (TEVA, AG1, AG MP-1M)
- Column size (1-20 mL)
- Washing solution (1-8 M HNO_3)
- Elution soultion (NH_2OHHCl-HCl, 0.1-1.0 M HCl)
- Flow rate (1-5 mL/min)

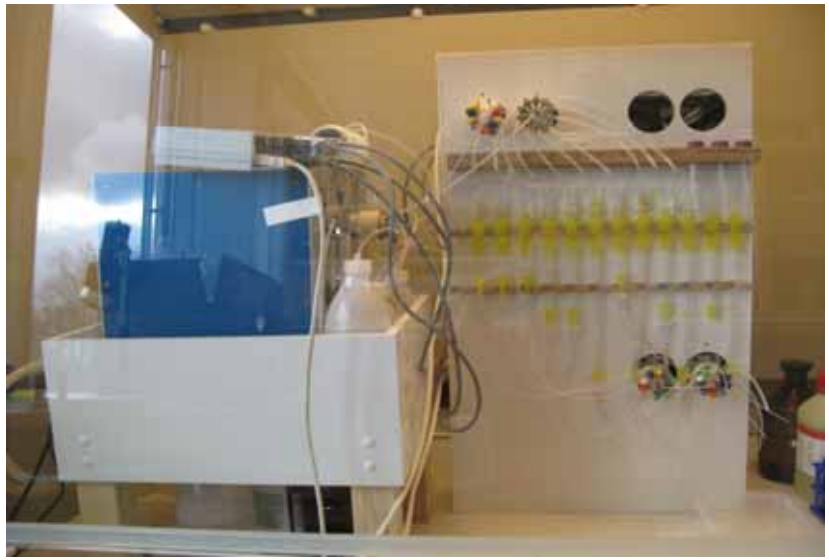
Performance evaluation :

Chemical yields; $^{237}Np/^{242}Pu$ chemical yield;

Decontamination of U; Method reability; Sample throughput

Auto-uint no.1---Sequential injection





Automatically handle 9 samples!
Work overnight !

Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytica Chimic Acta. 2011, 685, 111-119.

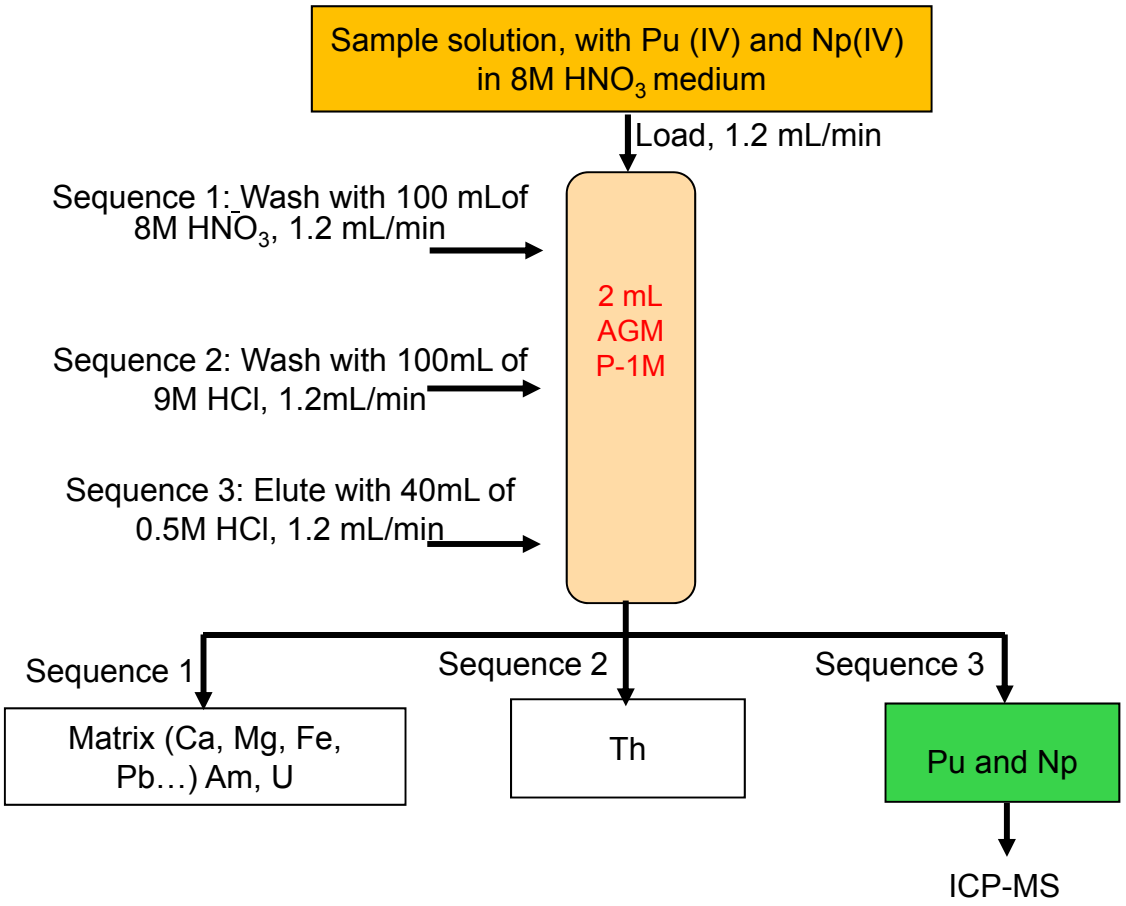
Selected results for soil analysis

Method	Analyte	Resin	Chemical yield of ^{242}Pu, Y_{Pu} (%)	Chemical yield of ^{237}Np, Y_{Np} (%)	Ration of Y_{Np}/Y_{Pu}	^{239}Pu measured (Bq/kg) *	^{240}Pu measured (Bg/kg)**	Decontamination factor ***		
								^{238}U	^{232}Th	^{208}Pb
Extraction chromato-graphy [1, 2]	Pu	TEVA (2mL, 0.7 × 5 cm)	97.7 ± 3.4	-	-	0.14 ± 0.01	0.09 ± 0.01	7.5×10^4	2.5×10^4	1.3×10^5
	Np & Pu	TEVA (2mL, 0.7 × 5 cm)	88.1 ± 3.4	85.7 ± 3.9	0.97	0.14 ± 0.01	0.09 ± 0.01	1.0×10^4	7.0×10^3	1.0×10^4
Anion chromato-graphy [3, 4]	Pu (&Np)	AG 1-X4 (50-100mesh), (2mL, 0.5 × 10cm)	103.0 ± 5.2	84.8 ± 5.3	0.75	0.14 ± 0.02	0.09 ± 0.01	3.9×10^3	2.4×10^4	2.7×10^4
		AG 1-X4 (100-200mesh), (2mL, 0.5 × 10cm)	91.6 ± 4.6	75.8 ± 4.6	0.77	0.14 ± 0.01	0.10 ± 0.01	6.9×10^3	1.7×10^4	1.0×10^3
	Np & Pu	AG MP-1M (100-200mesh), (2mL, 0.5 × 10cm)	86.5 ± 4.3	85.3 ± 4.3	0.99	0.14 ± 0.02	0.10 ± 0.01	3.9×10^3	2.5×10^5	1.0×10^3

10 g of soil was used in each analysis. *The reference value is 0.140 ± 0.008 Bg/kg. **The reference value is 0.098 ± 0.006 Bg/kg. *** The relative standard deviations were in all instances better than 10%.

1) Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytical Chemistry. 2009, 81, 8185-8192.
2) Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Journal of Analytical Atomic Spectrometry. 2010, 25, 1769-1779.
3) Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytica Chimica Acta. 2009, 652, 66-84.
4) Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Talanta. 2011, 84, 494-500.

Optimized chemical purification for Pu and Pu simultaneous determination



Loading: 0.2hr

Rinsing: 2.8hr

Pu elution: 0.5hr

Measurement : 0.5 hr (including sample preparation)

Comparison: >2 days using traditional method

Total: 3.5 + 0.5 = 4hr

Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytical Chemistry. 2011, 83, 374-381.

Performance comparison

Item	Extraction chromatography	Anion exchange chromatography
Price of resin	☹ High (e.g. 5600 €/500 g)	☺ Relatively Low (e.g. 330-1000 €/500 g)
Chemical yields	80-100% (Pu), ☹ 40-80% (Np&Pu)	☺ 80-100% (Pu), 70-90% (Np&Pu, AG MP-1M resin)
Separation time	☺ 1.5 hr/sample	☹ 2.5-3.5 hr/sample
Decontamination	☺ High (1-10 × 10^4 for ^{238}U)	☹ Medium (1-10 × 10^3 for ^{238}U)
Accuracy	☺ High (RSD ≤ 5%)	☹ Medium (RSD ≤ 10%)
Consumption of chemicals	☺ Low (e.g. 10 mL of conc. HNO_3/sample)	☹ High (e.g. 80 mL of conc. HNO_3/sample)
Recommendation	**Pu determination using TEVA resin**	**Pu &Np simultaneous determination using AG MP-1M resin**

Qiao, J. X. Risø-PhD-75 (EN), ISBN 978-87-550-3889-9, March 2011, Roskilde, Denmark.

Methods Development-Pu and Np

Biological samples:

- 1-5 L urine

Parameters optimized:

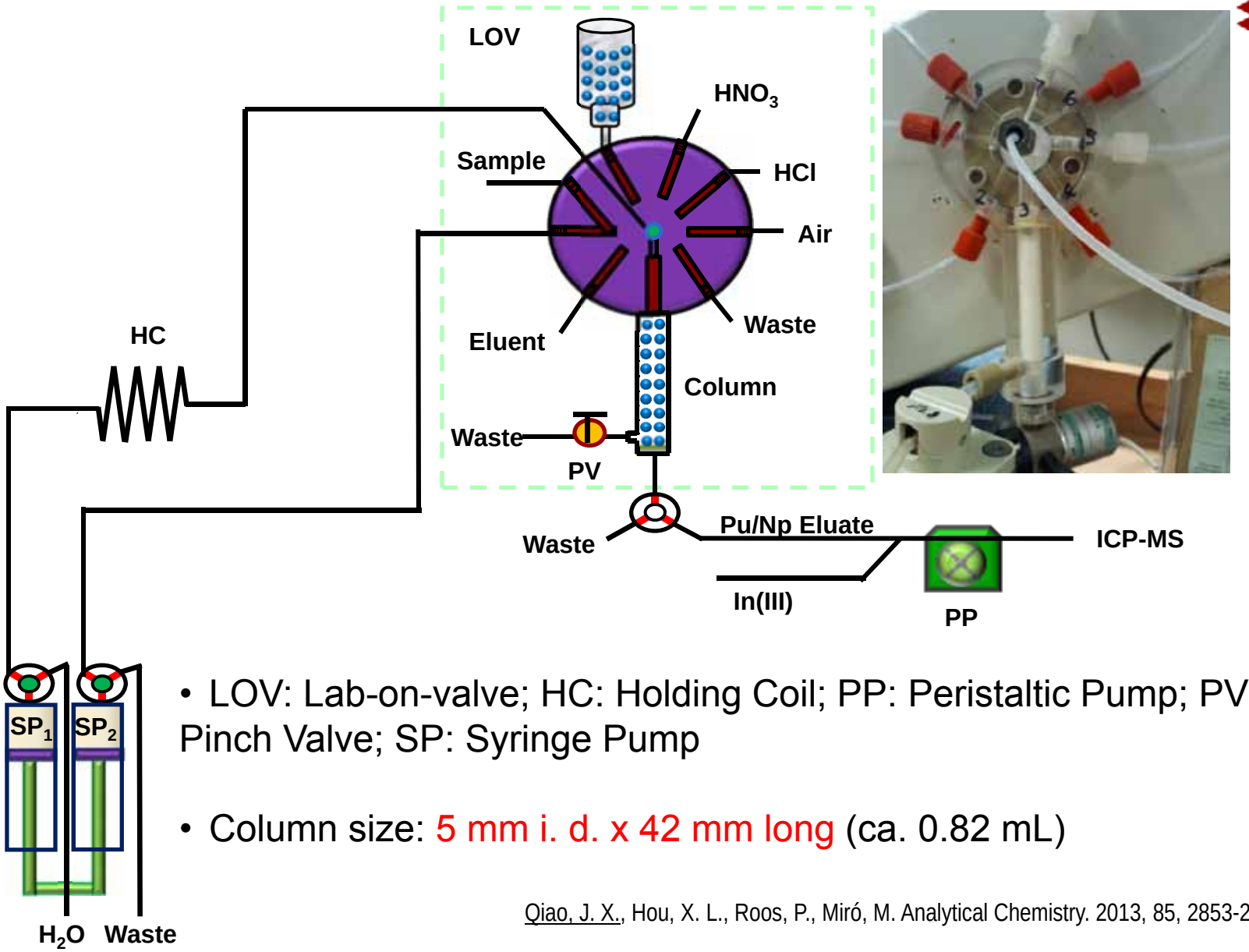
- Co-precipitation techniques ($Ca_3(PO_4)_3$, $Fe(OH)_3$, MnO_2, etc.)
- Decomposition of organic matter (acid digestion/dry ashing)
- Washing solution (0.2-1 M HNO_3)
- Elution soultion (0.025-0.5 M HCl)

Performance evaluation :

Chemical yields; $^{237}Np/^{242}Pu$ chemial yield ratio;

Method reability; Sample throughput

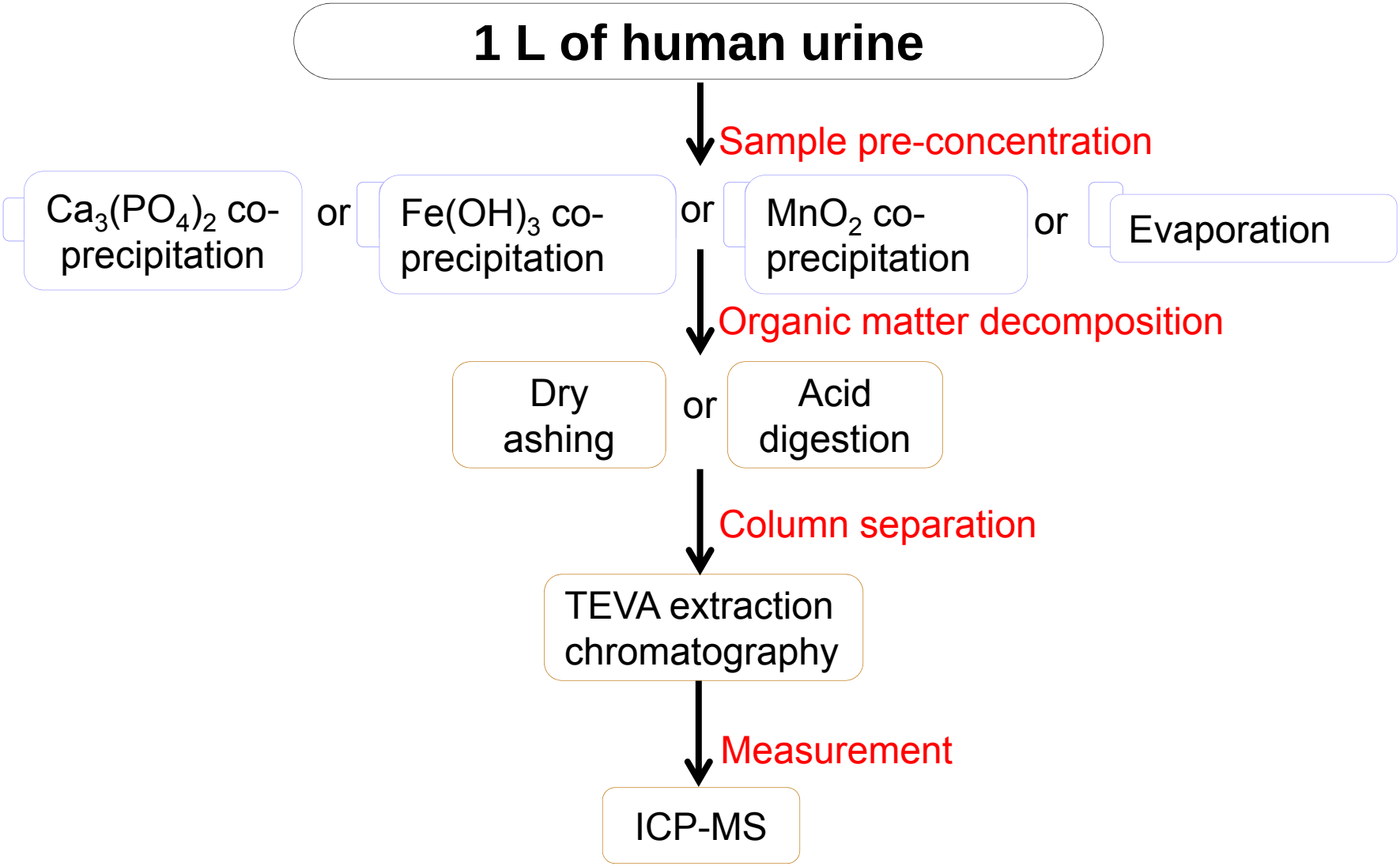
Auto-unit no.2---LOV bead injection



- LOV: Lab-on-valve; HC: Holding Coil; PP: Peristaltic Pump; PV: Pinch Valve; SP: Syringe Pump
- Column size: 5 mm i. d. x 42 mm long (ca. 0.82 mL)

Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytical Chemistry. 2013, 85, 2853-2859.

Analytical procedure for urine analysis



Selected results for urine analysis

Group no.	Pre-concentration method	Organic matter decomposition	Valence adjustment reagents	Operation time	Chemical yield		
					^{242}Pu,%	^{237}Np, %	^{237}Np/^{242}Pu
1	$Ca_3(PO_4)_2$ co-precipitation	Dry ash	Ascorbic acid / conc.HNO_3	13 hr	84.7 ± 5.7	80.9 ± 10.7	0.95
		Acid digestion		8 hr	46.8 ± 4.1	8.3 ± 5.4	0.18
2	$Fe(OH)_2/Fe(OH)_3$ co-precipitation	Dry ash	$Fe/K_2S_2O_5$ / conc.HNO_3	6 d	84.3 ± 15.6	73.3 ± 33.0	0.87
		Acid digestion		5.5 d	80.3 ± 9.9	77.9 ± 10.9	0.97
		Acid digestion		6 hr	51.3 ± 0.2	57.5 ± 8.8	1.12
3	**MnO_2 co-precipitation**	**Acid digestion**	**$Fe/K_2S_2O_5$ / conc.HNO_3**	**6 hr**	**88.4 ± 8.0**	**91.4 ± 10.0**	**1.03**
4	$Ca(OH)_2/Fe(OH)_2/Fe(OH)_3$ co-precipitation	Acid digestion	Ascorbic acid / conc.HNO_3	6 hr	87.3 ± 6.6	51.2 ± 1.6	0.59
5	Evaporation	Dry ash + acid leaching	$Fe/K_2S_2O_5$ / conc.HNO_3	1.5 d	75.5 ± 2.6	81.1 ± 3.6	1.07

Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytical Chemistry, 2013, 85, 1889-1895.

Methods Development-Pu, Np and U

Environmental Sample:

- 10 L of seawater

Parameters optimized:

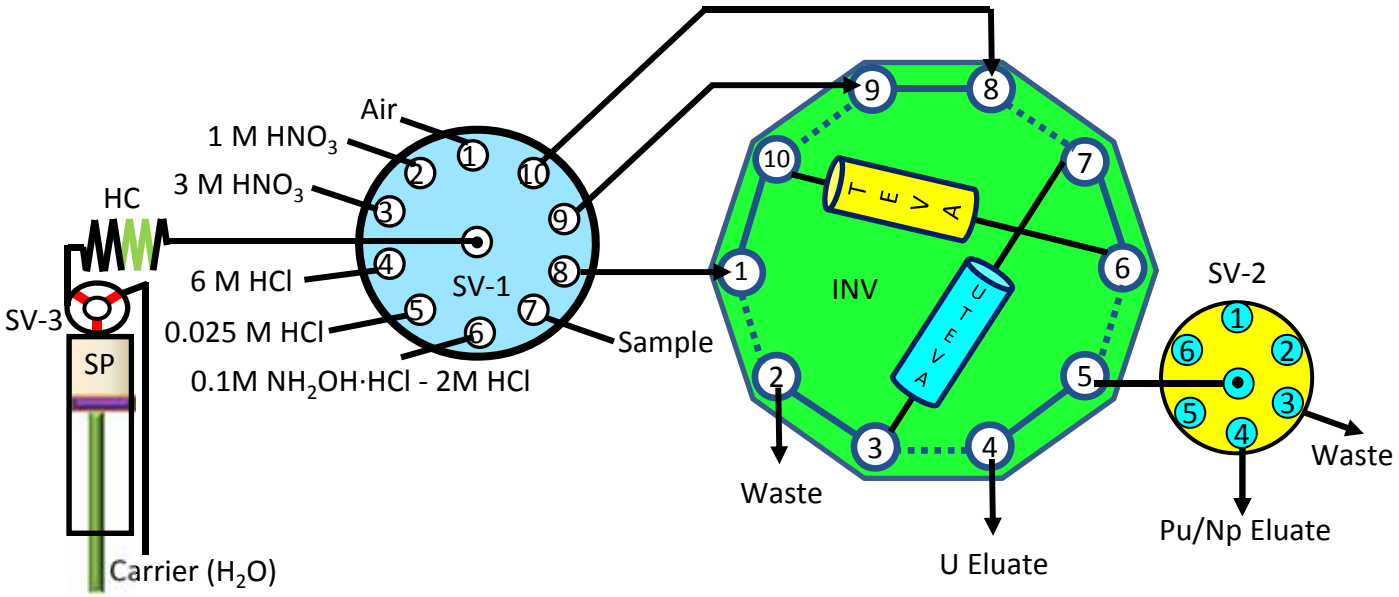
- Resin type (TEVA, UTEVA)
- Washing solution (1-4 M HNO_3)
- Decomposition of organic matter

Performance evaluation :

Chemical yields; $^{237}Np/^{242}Pu$ chemial yield ratio;

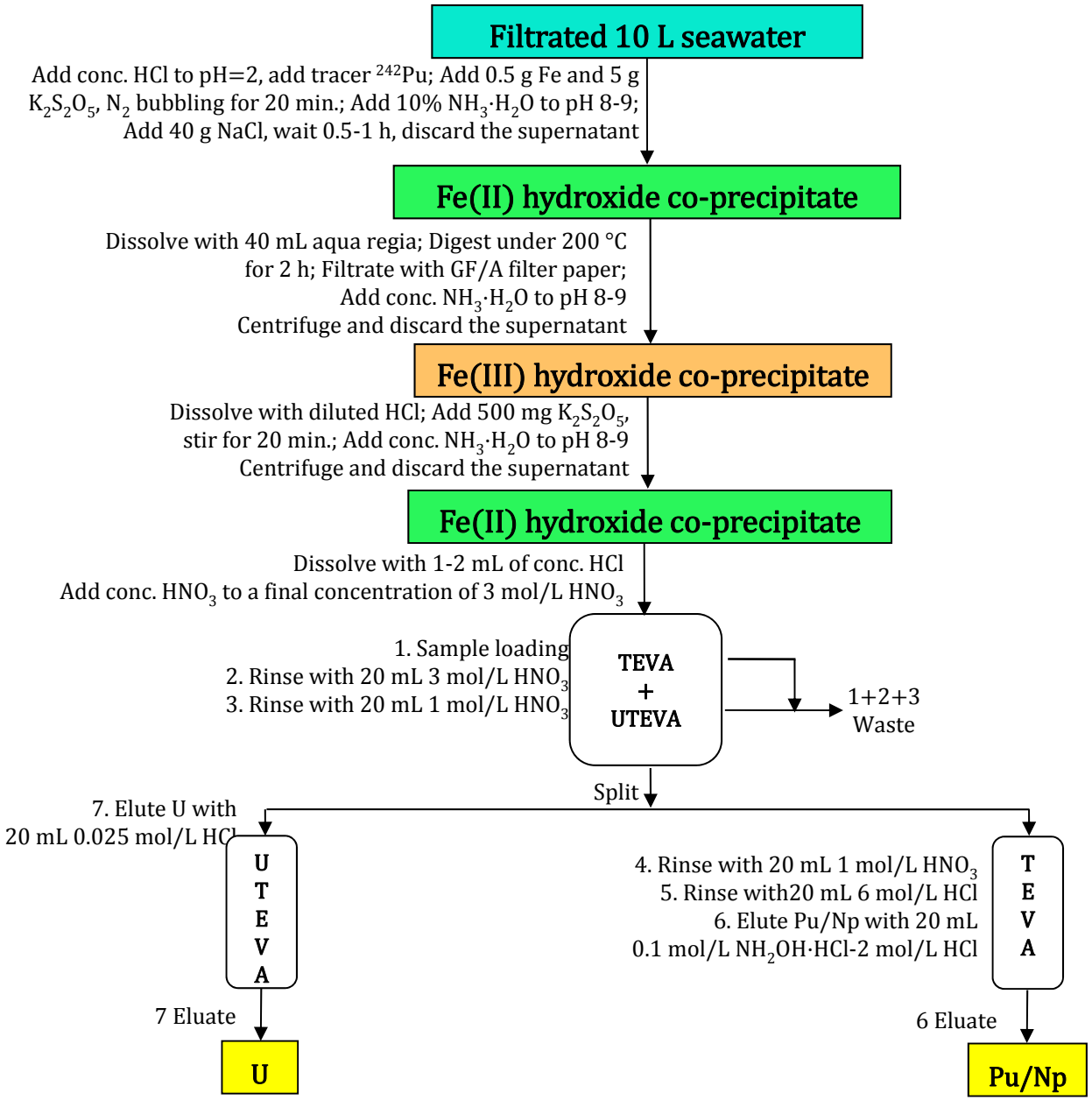
Method reability; Sample throughput

Auto-unit no.3---Dual-column sequential injection



Flexible control the connection of two columns!

Qiao, J. X., Hou, X. L., Steier, P., Golser, R. Analytical Chemistry. 2013, submitted.


Filtrated 10 L seawater
Add conc. HCl to pH=2, add tracer ^{242}Pu; Add 0.5 g Fe and 5 g $K_2S_2O_5$, N_2 bubbling for 20 min.; Add 10% $NH_3 \cdot H_2O$ to pH 8-9; Add 40 g NaCl, wait 0.5-1 h, discard the supernatant
Fe(II) hydroxide co-precipitate
Dissolve with 40 mL aqua regia; Digest under 200 °C for 2 h; Filtrate with GF/A filter paper; Add conc. $NH_3 \cdot H_2O$ to pH 8-9 Centrifuge and discard the supernatant
Fe(III) hydroxide co-precipitate
Dissolve with diluted HCl; Add 500 mg $K_2S_2O_5$, stir for 20 min.; Add conc. $NH_3 \cdot H_2O$ to pH 8-9 Centrifuge and discard the supernatant
Fe(II) hydroxide co-precipitate
Dissolve with 1-2 mL of conc. HCl
Add conc. HNO_3 to a final concentration of 3 mol/L HNO_3
1. Sample loading
2. Rinse with 20 mL 3 mol/L HNO_3
3. Rinse with 20 mL 1 mol/L HNO_3
TEVA + UTEVA
1+2+3 Waste
Split
7. Elute U with 20 mL 0.025 mol/L HCl
UTEVA
7 Eluate
U
4. Rinse with 20 mL 1 mol/L HNO_3
5. Rinse with20 mL 6 mol/L HCl
6. Elute Pu/Np with 20 mL 0.1 mol/L $NH_2OH \cdot HCl$-2 mol/L HCl
TEVA
6 Eluate
Pu/Np

Selected results for Pu/Np/U seawater analysis

Typical analytical performance					
Analytical time,	Chemical yield, %				DU
h	^{242}Pu	^{237}Np	^{237}Np/^{242}Pu ratio	^{238}U	
8	73.6±9.8	73.9±5.6	1.01±0.21	97.6±20.6	(5.3±0.5)×10^{4}

Method application with the use of AMS measurement

Sample ID	^{236}U/^{238}U, ×10^{-8}	^{238}U, μg/L	^{236}U atom/L,	Measured value, mBq/L		Expected value, mBq/L	
				^{237}Np	^{239}Pu	^{237}Np	^{239}Pu
North Atlantic-1	8.88 ± 1.33	2.76 ±0.41	(6.21 ± 0.93)× 10^{8}	<0.001	<0.005	-	-
North Atlantic-2	2.03 ± 0.30	2.17 ± 0.33	(1.11 ± 0.17)× 10^{8}	0.18	1.02	0.20	1.12
Roskilde Fjord-1	1.40 ± 0.21	1.65 ± 0.28	(6.88 ± 1.03)× 10^{7}	<0.001	0.03	-	-
Roskilde Fjord-2	1.65 ± 0.25	1.65 ± 0.28	(5.85 ±0.88)× 10^{7}	0.16	1.18	0.15	1.12

Methods Development-Pu, Np, U and Tc

Envrionmental Sample:

- 200 L of seawater

Parameters optimized:

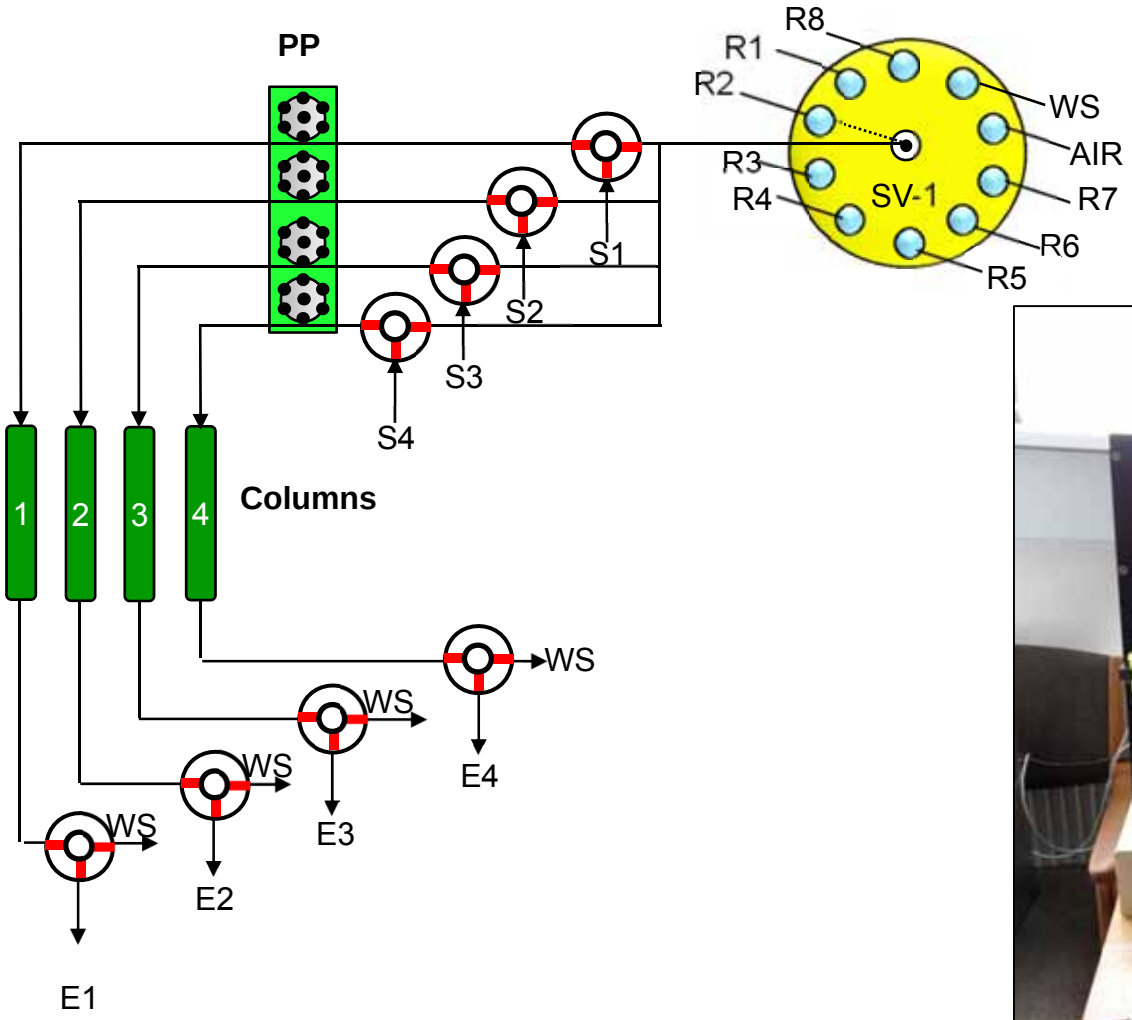
- Resin type (TEVA, UTEVA, AG MP-1M)
- Selection of Redox regents
- Decontamination of interferences

Performance evaluation :

Chemical yields; $^{237}Np/^{242}Pu$ chemial yield ratio;

Method reability; Sample throughput

Auto-uint no.4---Flow injection



Simultaneously handle 4 samples!

Qiao, J. X., Shi, K. L., Hou, X. L., Nielsen, S., Roos, P. Analytical Chemistry. 2013, in prep.

Summary

Objectives	Achievement
1. Rapid determination of Pu, Np, U and Tc	•Environmental solids: 2-5 h/sample •Large volume seawater: 1-2 days/sample •Biological samples: 6 h/sample
2. Automation of the analytical procedure	•Sample pre-concentration: batchwise •Chemical purification: automated 1. Auto-unit no.1: sequentially 9 samples 2. Auto-unit no.2: automated column packing 3. Auto-unit no.3: automated dual connection 4. Auto-unit no.4: simultaneously handle 4 samples •Measurement: automated

Conclusions and perspectives

Innovation of the previous work:

- Automatic
- Rapid and simple
- No need of Np isotopic tracer
- Low consumption of resins
- High sample throughput
- Low labor intensity

On-going projects:

- Tracer application studies of Pu and ^{236}U
- Multi-radionuclide determination (Pu/Np,U, Th, Am) in environmental samples

Thank you!

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